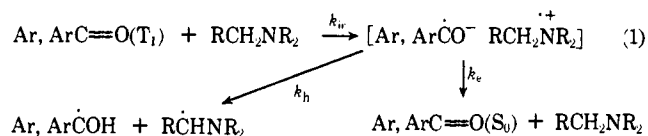# Photoreduction of π,π^* Triplets by Amines, 2-Naphthaldehyde, and 2-Acetonaphthone
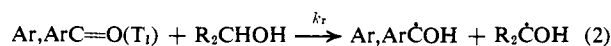
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Abstract: Photoreduction of 2-naphthaldehyde and 2-acetonaphthone by amines has been studied in acetonitrile, acetone, *tert*-butyl alcohol, benzene, and cyclohexane. Photoreduction by triethylamine in acetonitrile is efficient, φ = 1.2 and 0.7, respectively, and leads to the pinacols. Efficiency decreases with decreasing dielectric constant of solvent, and is very low in aliphatic hydrocarbons. Di-*n*-propylamine is less efficient than the tertiary amine; primary amines are essentially inert. 2-Naphthaldehyde is more reactive than 2-acetonaphthone throughout. Studies of 2-acetonaphthone and 2-naphthaldehyde as sensitizers for the dimerization of cyclohexadiene indicate similar yields of triplets in acetonitrile and hydrocarbons. Phosphorescence spectra of 2-naphthaldehyde are identical in hydrocarbon and ether–alcohol glasses and characteristic of π,π^* triplets. Effects of a quencher, piperylene, and of the concentration of amine have been studied. The rate constant for reaction of the naphthaldehyde triplet with triethylamine in acetonitrile is $\sim 8 \times 10^6$ M^{-1} sec^{-1}, while values in benzene and for 2-acetonaphthone in acetonitrile and in benzene are low, $\sim 1-6 \times 10^5$ M^{-1} sec^{-1}. Low rate constants for triplet deactivation, k_d, are also found. Aniline and DABCO do not photoreduce and do not quench effectively the photoreduction of the naphthyl carbonyl compounds. Reactions of π,π^* triplets with electron donors, which may lead to quenching or reduction, are favored by high triplet energy, low ionization potential of donor, and factors in the acceptor which stabilize negative charge.

The reduction and quenching of photoexcited aromatic ketones by amines have been described in a number of recent articles. Benzophenone,[1–3] acetophenone,[4] and 4-benzoylbenzoate ion[5] are photoreduced efficiently by primary, secondary, and tertiary amines. The reactions show low α-deuterium kinetic isotope effect, and low sensitivity to concentration of amine and to physical quenchers, and this insensitivity is greatest for tertiary amines. Nevertheless, quantum yields fall short of the maximum value of 2 which may be achieved in photoreduction by alcohols. These reactions may proceed[2,5] by initial rapid charge-transfer interaction, k_{ir}, followed either by transfer of α-hydrogen and formation of radicals, k_h, or by charge destruction and quenching k_e, eq 1. Low sensitivity to quenchers and

$$\text{Ar, ArC}{=}\text{O}(T_1) + \text{RCH}_2\text{NR}_2 \xrightarrow{k_{ir}} [\text{Ar, ArCO}^- \text{ RCH}_2\overset{\cdot+}{\text{NR}}_2] \quad (1)$$

$$\text{Ar, Ar}\overset{\cdot}{\text{C}}\text{OH} + \overset{\cdot}{\text{R}}\text{CHNR}_2 \qquad \text{Ar, ArC}{=}\text{O}(S_0) + \text{RCH}_2\text{NR}_2$$
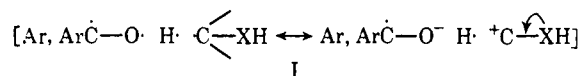
to concentration of amine may result from high values of k_{ir}. Quantum yields depend upon intersystem crossing efficiency and the relative magnitude of k_h and k_e. Alternatively, the reactions might proceed by two competing independent reactions of the triplet, direct abstraction of hydrogen from the amine, and quenching by amine. The two mechanisms lead to similar formal kinetic schemes. In the second, k_{ir} would be defined as the sum of the rate constants for abstraction and quenching. In photoreduction by alcohols, specific quenching of triplets by the alcohol is generally not important, and direct abstraction occurs, k_r, eq 2. The

$$\text{Ar,ArC}{=}\text{O}(T_1) + \text{R}_2\text{CHOH} \xrightarrow{k_r} \text{Ar,Ar}\overset{\cdot}{\text{C}}\text{OH} + \text{R}_2\overset{\cdot}{\text{C}}\text{OH} \quad (2)$$

quantum yield depends on the ratio of reduction to deactivation of the triplet, $k_r(\text{RH})/k_d$, and on efficiency of intersystem crossing. Abstraction of hydrogen from alcohols may be facilitated by a polar contribution to the transition state, formula I.[2] The nitrogen of amines

$$[\text{Ar, Ar}\overset{\cdot}{\text{C}}{-}\text{O}\cdot\ \text{H}\cdot\ \text{C}{\lessgtr}\text{XH} \longleftrightarrow \text{Ar, Ar}\overset{\cdot}{\text{C}}{-}\text{O}^-\ \text{H}\cdot\ ^+\text{C}{\lessgtr}\text{XH}]$$
$$\text{I}$$

may also facilitate abstraction of hydrogen in this way. The two mechanisms differ in the relative extents of transfer of electron and hydrogen, and there may be cases and conditions in which they merge.[4]

Amines may photoreduce ketones which are not photoreduced by alcohols: *p*-aminobenzophenone, PAB, is photoreduced by tertiary amines in nonpolar media, but not in polar solvents, and not at all by primary amines.[6] Fluorenone triplet is photoreduced while the excited singlet is quenched by many amines.[7,8] Both the singlet and triplet of biacetyl are quenched by amines.[9] It has been noted that 2-acetonaphthone is photoreduced by triethylamine, TEA.[7] Naphthyl carbonyl compounds have the lowest π,π^* triplet states,[10–12] which show little if any activity in photoreduction by alcohols[13,14] and in oxetane formation,[15,16] and are photoreduced by tri-*n*-butylstannane.[14] It was of interest to study the reactions of the π,π^* triplets of 2-acetonaphthone, 2-AN, and 2-naphthaldehyde, 2-NA, with amines, since, unlike the reactions of fluorenone,[7,8]

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and PAB,[17] these might not be complicated by singlet quenching and solvent-dependent intersystem crossing.

Experimental Section

Materials. 2-Naphthaldehyde (Aldrich) was crystallized from hexane, mp 59–60°. 2-Acetonaphthone (Eastman) was crystallized from hexane, mp 59–61°. Triethylamine, cyclohexylamine, 2-butylamine, di-*n*-propylamine, benzene (Spectrograde), and *tert*-butyl alcohol, were obtained from Eastman and distilled. Diazabicyclooctane, DABCO (Aldrich), was crystallized from benzene–petroleum ether (30–60°) and sublimed *in vacuo*. Quinuclidine, ABCO (Aldrich), was treated with NaOH, extracted into benzene, dried, concentrated, and sublimed at 158–161°. Piperylene (Aldrich), a mixture of cis and trans isomers, and cyclohexadiene (Aldrich) were distilled. Acetonitrile (Matheson Coleman and Bell, Spectro quality), isooctane (Fisher, Spectra analyzed), cyclohexane, and acetone (Fisher, AR) were distilled. For emission and flash photolysis experiments, fluorescent grade benzene (Eastman), ethyl alcohol (U.S.I., USP-NF grade), and anhydrous ether (Fisher) were used.

Irradiation Procedures. Solutions of carbonyl compound, amine, and solvent, 3 or 5 ml, in square Pyrex tubes fitted with Fisher-Porter Teflon screw closures, were degassed in three freeze–pump–thaw cycles at 0.05 mm. Quantum yields were determined with irradiation at 313 and 334 nm on a Bausch and Lomb monochromator by ferrioxalate actinometry.[18] Solutions of the carbonyl compounds and the several amines in acetonitrile, solutions of the carbonyl compounds with varying concentrations of triethylamine in the several solvents, solutions of the carbonyl compounds, triethylamine, and varying concentrations of added quencher, piperylene, were irradiated on a rotating wheel about a G. E. H-85W-A3 Hg lamp. Rates of reduction were determined from the absorbance of the carbonyl compounds after timed intervals, determined with a Beckman DU or Cary 14 spectrophotometer. For 2-naphthaldehyde an absorption peak at 343 nm was used (ϵ 2340) in benzene. For 2-acetonaphthone an absorption peak at 340 nm was used (ϵ 1700). Corrections were applied for the fraction of light absorbed, and for absorption by the products. Plots of per cent reaction against time were linear for the first 25% reaction. The carbonyl compounds were essentially not photoreduced by the solvents.

Phosphorescence emission spectra were determined on a Farrand Mark I spectrofluorimeter. Aliquots, 3 ml, of 10^{-2}–10^{-3} M 2-naphthaldehyde in Pyrex or quartz tubes fitted with Teflon closures were evacuated by the freeze–thaw procedure at 1.5–3.0 μ, for experiments at 77°K. Phosphorescence lifetimes of 2-naphthaldehyde in degassed rigid media at 77°K were determined by a simplified flash photolysis technique.[19]

Triplet yields were estimated by quenching of excited 2-acetonaphthone and 2-naphthaldehyde by cyclohexadiene and analysis for cyclohexadiene dimers.[20] Solutions of 0.40 M cyclohexadiene and 0.10 M 2-acetonaphthone in cyclohexane, benzene, *tert*-butyl alcohol, and acetonitrile were degassed in Pyrex tubes and irradiated on the wheel for a period of 20 min. Nmr spectra were obtained and the decrease in the vinylic absorption, δ 5.75, and allylic absorption, δ 2.0, of cyclohexadiene relative to the unchanging methyl singlet of acetonaphthone at δ 2.68 led to the extent of dimerization. Solutions of 0.10 M 2-naphthaldehyde and 0.40 M cyclohexadiene in cyclohexane and in acetonitrile were degassed and sealed in nmr tubes and irradiated on the wheel for timed intervals. Relative intensities of the decreasing olefinic and the constant aromatic absorptions at δ 5.75 and 7.3–8.1, respectively, led to values of the extent of dimerization.

Naphthaldehyde Pinacol. (i) Solutions of 0.20 g of 2-naphthaldehyde and 1 ml of triethylamine in 5 ml of benzene or *tert*-butyl alcohol in capped Pyrex tubes were irradiated under nitrogen for 5 hr with the G.E. lamp. A precipitate formed and was collected: the diastereomeric pinacols, 0.08 g, 40% yield in benzene, mp 242–248°, and 0.10 g, 50% yield in *tert*-butyl alcohol, mp 225–237°. The solvent was removed from each filtrate and the residue was

examined by ir and nmr. Only pinacol and residual 2-naphthaldehyde appeared to be present. (ii) Solutions of 0.5 g of 2-naphthaldehyde and 3 ml of triethylamine in 100 ml of solvent, benzene, acetonitrile, *tert*-butyl alcohol, or acetone, were irradiated under nitrogen for 22 hr. The mixed pinacols were obtained in 20–30% yield, melting 240–255°. The *meso*-pinacol[21] melts at 261–262° and the *dl*-pinacol[21] melts at 220–222°.

A solution of 0.10 g of the isolated pinacol mixture in 5 ml of dioxane was added to 0.5 g of NaIO₄ and 4 drops of HNO₃ in 5 ml of water. The mixture was stirred and heated at 65° for 10 min, cooled, diluted with water, and extracted with ether, leading to a solid residue, 0.091 g, mp 54–57°, with the ir spectrum virtually identical with that of 2-naphthaldehyde, mixture mp 58–60°.

(iii) Solutions of 0.5 g of 2-naphthaldehyde and 1 ml of tributylstannane[22] in 10 ml of cyclohexane, benzene, or *tert*-butyl alcohol were irradiated and led to the pinacol in about 20% yield in each case. Melting and mixture melting points were in the 240–255° range.

2-Acetonaphthone Pinacol. (i) A solution of 0.30 g of 2-acetonaphthone and 1 ml of triethylamine in 5 ml of acetonitrile was irradiated for 24 hr and concentrated *in vacuo*, and the residue was chromatographed on Merck acid-washed alumina. 2-Acetonaphthone was recovered, 0.05 g, mp 55–59°, mmp 58–59°, and then the pinacol, 2,3-di(2-naphthyl)-2,3-butanediol, 0.050 g, mp 188–192°, from ether–petroleum ether (lit. mp 158–171°,[23] 184°[24]). The infrared spectrum in CHCl₃ showed a hydroxyl band at 2.8 μ, with a shoulder at 2.9 μ. The nmr spectrum in CDCl₃ showed a complex aromatic multiplet at δ 7.2–8.0, broad hydroxyl singlets at 2.4 and 2.8 in a ratio of 3:1, and sharp methyl singlets at 1.70 and 1.62 in a ratio of 3:1 to each other and to the corresponding hydroxyl absorptions. The spectrum indicated a 3:1 mixture of the diastereomeric pinacols; the spectrum of the semisolid residue after removal of the crystallization liquors, 0.16 g, showed the same features with absorptions at δ 2.8 and 1.62 being greater than those at 2.4 and 1.70 by a factor of 2:1. A portion of this product, 0.15 g, was oxidized at 60–70° for 5 min with 0.5 g of NaIO₄ in 0.5 ml of water and 5 ml of dioxane containing a few drops of nitric acid. This led to 0.12 g of crude acetonaphthone, with a carbonyl band at 5.98 μ, an infrared spectrum like that of 2-acetonaphthone, and an nmr singlet at δ 2.68.

(ii) Solutions of 0.20 g of 2-acetonaphthone and 0.5 ml of TEA in 5 ml of *tert*-butyl alcohol, acetonitrile, or benzene were irradiated for 15 hr, and the solvent was removed; nmr spectra of the crude residues indicated the formation of approximately equal amounts of the diastereomeric pinacols in each solvent. Consideration of the areas of the total aromatic multiplet, the pinacol methyls, δ 1.62 and 1.70, and the remaining acetonaphthone methyl 2.68, indicated that the pinacols accounted for ~90% of the reduced ketone. The crude products were extracted with dilute acid, the extract was made basic and extracted with ether, and the ether extract was concentrated, leading to a small oily residue. The nmr and infrared spectra were consistent with this being the cross-coupling product 2-(2-naphthyl)-2-hydroxy-3-diethylaminobutane.

(iii) A solution of 1.0 g of 2-acetonaphthone and 1.5 ml of tri-*n*-butylstannane in 50 ml of benzene was irradiated for 24 hr, chromatographed on Florisil, and crystallized, leading to unreduced acetonaphthone, to a small quantity of the pinacol, mp 170–180°, and to much 2-naphthylmethylcarbinol,[14] with a methyl doublet at δ 1.4 and 1.5 and an α-H quartet centering at 5.0.

Results

In preliminary experiments a survey was made of the reactivity of 0.005 M 2-naphthaldehyde, NA, and of 0.006 M 2-acetonaphthone, AN, toward photoreduction by 0.07 M solutions of primary, secondary, and tertiary amines in a polar solvent, acetonitrile. Degassed solutions of each carbonyl compound were irradiated simultaneously on the wheel and rates of photoreduction were measured. Only a tertiary amine, triethylamine, led to rapid photoreduction, and the alde-

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hyde was about twice as reactive as the ketone. A secondary amine, di-n-propylamine, was about 0.15 as reactive as the tertiary amine toward 2-NA, and 0.05 as reactive toward 2-AN. Primary amines, cyclohexylamine and 2-butylamine, and bridged bicyclic tertiary amines, quinuclidine and DABCO, showed very low reactivity.

In preparative experiments irradiation of solutions of the carbonyl compound and triethylamine in benzene, tert-butyl alcohol, acetonitrile, or acetone led to the meso- and dl-pinacols. The pinacol of 2-naphthaldehyde crystallized directly, in good yield, from the irradiations in benzene and tert-butyl alcohol. 2-Naphthylcarbinol did not appear to be formed. Photoreduction by tri-n-butylstannane was less efficient. meso- and dl-pinacols were formed in approximately equal yields from photoreduction of 2-acetonaphthone by triethylamine in acetonitrile. Again the monomolecular reduction product, 2-naphthylmethylcarbinol, did not appear to be formed, while it was the major product of photoreduction by tri-n-butylstannane in benzene. The cross-coupling product, 2-(2-naphthyl)-2-hydroxy-3-diethylaminobutane, appeared to be formed in low yield in the photoreduction by triethylamine. The two pairs of pinacols were characterized, in part, by oxidation by periodic acid to the starting carbonyl compounds.

Quantum yields were determined by ferrioxalate actinometry[18] for photoreduction of 2-naphthaldehyde and 2-acetonaphthone by ~ 0.1 M triethylamine at 313 nm in a series of solvents. 2-Naphthaldehyde shows high quantum efficiency in the dipolar solvents acetonitrile and acetone, $\varphi = 1.2$ and 1.0, respectively, lower efficiency in tert-butyl alcohol and benzene, $\varphi = 0.6$ and 0.4, respectively, very low quantum yield, $\varphi < 0.05$, in cyclohexane, and little if any photoreduction by TEA in isooctane. N,N-Dimethylaniline showed similar efficiency to triethylamine in the photoreduction of 2-naphthaldehyde in benzene. 2-Acetonaphthone shows a moderately high quantum yield in photoreduction by TEA in acetonitrile, $\varphi = 0.7$, lower reactivity in tert-butyl alcohol, $\varphi = 0.1$, and benzene, $\varphi = 0.04$, and very little if any reactivity when irradiated in 0.05–0.50 M TEA in cyclohexane.

Because of this marked effect of solvent on photoreduction by triethylamine, the effect of the solvents on the yield of triplets was assessed by the study of 2-acetonaphthone and 2-naphthaldehyde as sensitizers for the dimerization of 1,3-cyclohexadiene, for which a quantum yield of 1.0 is reported.[25] Extents of conversion to the dimer were measured by nmr. Solutions of 0.10 M 2-acetonaphthone and 0.40 M 1,3-cyclohexadiene in four solvents, cyclohexane, benzene, acetonitrile, and tert-butyl alcohol, were irradiated, for 20 min. The yields of triplet, as indicated by the 60–70% yields of dimer, were high and essentially the same in the hydrocarbons and in the dipolar acetonitrile, in which the rates of photoreduction by TEA were most different. tert-Butyl alcohol appeared to show an intermediate value of both triplet yield, as indicated by 30% yield of dimer, and of photoreduction quantum yield. Solutions of 0.1 M 2-naphthaldehyde and 0.40 M cyclohexadiene in cyclohexane and in acetonitrile were ex-

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amined for dimer content as a function of irradiation time. Rates of dimerization were followed to 60% yield of dimer and were identical in the two solvents. Thus, rates of formation of triplet were probably the same in the two solvents, but rates of photoreduction were very different.

The emission spectra of 2-naphthaldehyde in 1:1 isohexane-cyclohexane and in 1:1 ether-alcohol at 77°K were obtained. Identical phosphorescence emission was displayed in the hydrocarbon and polar media, sharp bands at 478 and 516 nm, shoulders at 487 and 503 nm, and a broader band at 550 nm. Phosphorescence lifetimes of 2-naphthaldehyde triplet were measured in the two media by flash photolysis.[19] Lifetimes of 0.25 and 0.31 sec were obtained in the hydrocarbon and ether-alcohol matrices, respectively. These values are in satisfactory agreement with values of 0.35 sec[12] and 0.25 sec[11] reported in ether-alcohol and etherpentane-alcohol, respectively, and support the π,π^* configurational assignment of the lowest triplet at 77°K. Solvent did not seem to affect the character or configuration of the triplet at low temperature. We observed no emission from solutions of 2-naphthaldehyde in benzene, cyclohexane, tert-butyl alcohol, or acetonitrile at room temperature.

Rates of photoreduction of 2-naphthaldehyde and 2-acetonaphthone by triethylamine were examined in acetonitrile, tert-butyl alcohol, and benzene, at 313 or 334 nm, with 0.0005 and 0.006 M carbonyl compound and 0.01–1.0 M amine. Rates, which were the same at the two wavelengths, were converted to quantum yields. Inverse plots of quantum yield against concentration of amine were constructed. Results are summarized in Table I.

Table I. Photoreduction of 2-Naphthaldehyde, 2-NA, and 2-Acetonaphthone, 2-AN, by Triethylamine

Solvent	Compd	Slope, M^a	Intercept^a	$\varphi_{lim}{}^b$
Acetonitrile	2-NA	~ 0.0005	0.85	1.2
tert-Butyl alcohol	2-NA	0.0053	1.6	0.63
Benzene	2-NA	0.025	2.15	0.46
Acetonitrile	2-AN	0.015	1.5	0.67
tert-Butyl alcohol	2-AN	0.03	6.2	0.16
Benzene	2-AN	~ 1.5	~ 20	0.05

^{a} Of plots of $1/\varphi$ via $1/[RH]$. ^{b} Reciprocal of intercept.

The dipolar solvent, acetonitrile, leads to lower slopes of the inverse plots, characteristic of high rates of interaction of the ketone triplet with the amine. The hydrocarbon solvent shows low quantum yields and larger values of the slopes, characteristic of lower values of k_{ir}. Photoreduction of 2-naphthaldehyde is in all respects more efficient than that of 2-acetonaphthone.

Quenching by piperylene of the photoreduction of the naphthyl carbonyl compounds by 0.24 M triethylamine in acetonitrile and in benzene was studied. Results are summarized in Figures 1 and 2, plots of φ_0/φ, ratios of unquenched to quenched rates of photoreduction, against concentration of piperylene. For 2-naphthaldehyde the slope is 200 M^{-1} in acetonitrile and 3000 M^{-1} in benzene. The quencher is 15-fold more efficient in benzene indicating that k_{ir} is substantially greater in acetonitrile than in benzene. For 2-acetonaphthone the slope is 2600 M^{-1} in acetonitrile and 9000 M^{-1} in benzene. The larger values of the slopes for 2-aceto-
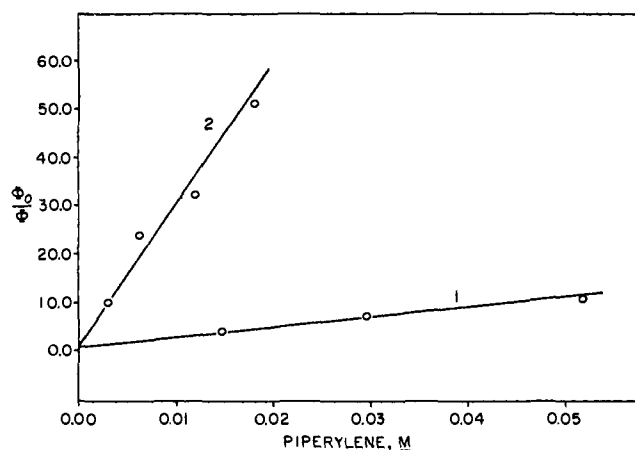
Figure 1. Quenching by 0.002–0.05 M piperylene of photoreduction of 2-naphthaldehyde by 0.24 M triethylamine: curve 1, 0.0006 M NA in acetonitrile; curve 2, 0.0007 M NA in benzene.

Figure 2. Quenching by 0.0002–0.005 M piperylene of photoreduction of 2-acetonaphthone by 0.24 M triethylamine: curve 1, 0.0007 M AN in acetonitrile; curve 2, 0.0006 M AN in benzene.

naphthone indicate that values for k_{ir} are less than for 2-naphthaldehyde, and again k_{ir} is greater in acetonitrile than in benzene.

Attempts were made to study quenching by cyclohexadiene. It was very efficient, but plots like those of Figures 1 and 2 showed curvature, a fall-off in slope with increasing concentration, possibly because of sensitized dimerization and disappearance of the quencher. In one experiment, in irradiation of 0.0005 M 2-acetonaphthone and 0.25 M triethylamine in acetonitrile, the initial slope of the plot of φ_0/φ vs. concentration of cyclohexadiene was 38,000 M^{-1} indicating 15-fold greater efficiency of quenching by cyclohexadiene than by piperylene.

Certain amines, which do not photoreduce fluorenone well, quench the triplet and retard photoreduction of fluorenone by triethylamine.[26] Two such amines, aniline and 1,4-diazabicyclooctane, DABCO, were examined as retarders of the photoreduction of the naphthylcarbonyl compounds. DABCO, 0.087 M, had no quenching effect on the photoreduction of 0.005 M 2-naphthaldehyde by triethylamine, 0.066 M and 0.045 M in acetonitrile, and benzene, respectively. At 0.17 M, DABCO had a small retarding effect in benzene, $\varphi_0/\varphi = 1.2$, corresponding to $k_q/k_{ir} \sim 0.05$. Aniline, 0.029 M, had a small retarding effect in acetonitrile, possibly corresponding to $k_q/k_{ir} \sim 0.1$. In the less-efficient photoreduction by a secondary amine, 0.05 M di-n-propylamine in acetonitrile, 0.086 M DABCO showed stronger retardation, $\varphi_0/\varphi = 7.6$, corresponding to $k_q/k_{ir} = 4$. In the photoreduction of 2-acetonaphthone by 0.05 M triethylamine in acetonitrile, aniline showed some retardation, $\varphi_0/\varphi = 1.35$, corresponding to $k_q/k_{ir} = 1$. Aniline and DABCO are far less efficient quenchers for the naphthyl compounds than for fluorenone,[26] and are far less efficient than piperylene. The 11-fold difference in effect of aniline on the two carbonyl compounds is similar to the difference in the effect of piperylene on them.

Discussion

2-Naphthaldehyde and 2-acetonaphthone may be photoreduced efficiently by a tertiary amine, with lower efficiency by a secondary amine, and little if at all by

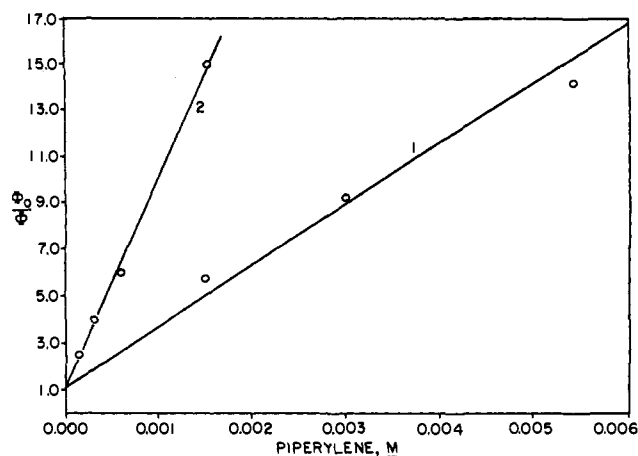(26) G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1970).

primary amines. This behavior is similar to that of fluorenone[7,8] and p-aminobenzophenone,[6] and may be characteristic of ketones with low-lying π,π^* triplets. Aromatic ketones with n,π^* triplets are photoreduced well by all amines which have hydrogen on the α-carbon. π,π^* triplets may require the lower ionization potentials of tertiary amines or they may undergo more quenching on interaction with the –ṄH– group of secondary and primary amines. The naphthyl carbonyl compounds are not photoreduced by the bicyclic tertiary amines, DABCO and quinuclidine, despite the low ionization potentials. p-Aminobenzophenone[6] and fluorenone[26] are photoreduced by DABCO with moderate and low quantum yields. Photoreduction by the bridgehead amine may be more difficult than by triethylamine, because the polar contribution to the transition state, formula I, is of less assistance because of geometrical restriction. p-Aminobenzophenone has high-triplet energy, 67 kcal,[27] and forms a stable diarylketyl radical. Fluorenone has low-triplet energy, 53 kcal,[28] but has high ketyl radical stability and unusually high stability of the anionic component of the polar contributor to the transition state. The low reactivity of the naphthyl compounds may be due to low stability of the radical or radical anion, and moderate triplet energy, $\sim$59 kcal,[28] added to the π,π^* triplet character.

Quantum yields for photoreduction by triethylamine of the π,π^* triplets of the naphthyl carbonyl compounds are high in the dipolar aprotic solvents acetonitrile and acetone, and decrease with decreasing dielectric constant in the hydroxylic solvent, *tert*-butyl alcohol, and the hydrocarbon, benzene, and are very low in aliphatic hydrocarbons. A high dielectric constant may increase the quantum yield if it favors formation of the CT complex k_{ir}, eq 1, or increases k_r by favoring the polar contribution to the transition state, eq 2. This solvent effect is similar to the effect on the rate constants for quenching by amines of the luminescence of the n,π^* excited states of biacetyl.[9] In that case it was also attributed to the effect on the charge-transfer interaction. Solvent may also affect efficiency of intersystem crossing. The sensitized dimerization of 1,3-cyclohexadiene indicates that the yields of triplets are the same in the

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hydrocarbon and in acetonitrile, and that the low quantum yields for photoreduction of the naphthyl compounds in hydrocarbon solvents are not related to intersystem crossing effects. A triplet yield of 0.84 has been reported for 2-acetonaphthone in benzene.[29] However, tert-butyl alcohol appears to decrease triplet yield and quantum yield. Fluorenone, on the other hand, has shown decreased yield of triplet in acetonitrile and very low yield in 2-propanol, as compared with hydrocarbon and low photoreduction by triethylamine in these solvents.[30] However, addition of a little acetonitrile to the hydrocarbon solvent increased quantum yield, possibly by affecting k_{ir} after the triplet is formed in the nonpolar medium. p-Aminobenzophenone also showed a decreased yield of triplet in acetonitrile and very low yield in 2-propanol as compared with hydrocarbon,[17] accounting for the failure of this ketone to be photoreduced by alcohols and by triethylamine in polar solvents.[6] Benzophenone shows simpler behavior, with intersystem crossing[17] and hydrogen abstraction[5] relatively insensitive to solvent. However, formation of light-absorbing transients increased in polar solvents[6] and decreased observed quantum yields.

The quantum yield for photoreduction of 2-naphthaldehyde by triethylamine in acetonitrile is significantly greater than 1, indicating that a second reducing group is transferred from the amine-derived radical to ground-state ketone, eq 3. The enamine has been

$$Ar,ArC{=}O + CH_2\dot{C}HNR_2 \longrightarrow$$

$$Ar,Ar\dot{C}OH + CH_2{=}CHNR_2 \quad (3)$$

characterized in photoreduction of benzophenone by triethylamine.[31] The pinacols are the major products of the photoreduction, and only a little of the mixed coupling product, which might be formed in substantial yields if the amine derived radical persisted, appears to be formed. While the lower quantum yields in the other solvents do not require transfer of a second hydrogen, they may result largely from less efficient abstraction of the first hydrogen, due to diminished polar contributions in the nonpolar solvents.

The dependence of quantum yield for photoreduction on concentration of amine may be indicated by eq 4;

$$1/\varphi = 1/af + k_d/afk_{ir}[Am] \quad (4)$$

a may include the fractional triplet yield and the contribution of the second reducing step, eq 3, and have a maximum value of 2; f is the fraction of reaction of triplet with amine which leads to hydrogen abstraction, the remainder leading to quenching, and has the maximum value of 1; k_{ir} is the rate constant for the total reaction of triplet with amine, the rate constant for formation of the charge-transfer complex, eq 1, or the sum of rate constants for reaction with and quenching by amine if two independent processes occur. The ratio of slope to intercept of plots of $1/\varphi$ vs. $1/[AM]$ is k_d/k_{ir}, where k_d is the rate constant for self- and solvent-induced deactivation of triplet. Values of this ratio are given in Table II. For 2-naphthaldehyde the low values of k_d/k_{ir} indicate that the initial interaction is efficient, and that quantum yields less than the maximum value

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Table II. Photoreduction of 2-Naphthaldehyde, 2-NA, and 2-Acetonaphthone, 2-AN, by Triethylamine in Acetonitrile, tert-Butyl Alcohol, and Benzene

Solvent	Compd	k_d/k_{ir}, M	k_q/k_{ir} [a]	k_{ir}(est),[b] M^{-1} sec^{-1}	k_d,[c] sec^{-1}
Acetonitrile	2-NA	~0.0006	50	8×10^8	5×10^3
tert-Butyl alcohol	2-NA	0.0033			
Benzene	2-NA	0.012	750	5×10^5	6×10^3
Acetonitrile	2-AN	0.010	650	6×10^5	6×10^3
tert-Butyl alcohol	2-AN	0.005			
Benzene	2-AN	0.07	2800	1×10^5	7×10^3

[a] For quenching by piperylene. [b] Estimate based on $k_q = 4 \times 10^8$ M^{-1} sec^{-1} for quenching by piperylene. [c] Based on values of k_d/k_{ir} and the estimated k_{ir}.

of 2 arise from factors affecting a and f. In acetonitrile small inefficiencies in intersystem crossing and the reaction of eq 3 and partial quenching of triplet by amine may account for the less than perfect quantum yield. Since intersystem crossing is the same in acetonitrile and benzene, the low quantum yield in benzene is due in part to the less favorable k_d/k_{ir} ratio, and largely to failure of the polar effect to assist transfer of hydrogen, k_h, in the nonpolar solvent. Thus, quenching by the amine, k_e, becomes more important. For 2-acetonaphthone, lower stability of the radical anion component of the initial CT complex leads to low k_{ir}, and probably also to an unfavorable ratio of k_h to k_e and thus to a higher proportion of quenching of triplet by amine. The very inefficient photoreduction in benzene shows a marked dependence on concentration of amine, and a high value of k_d/k_{ir}, observed for the first time in photoreduction by an amine.

The dependence of quantum yield for photoreduction on concentration of added quencher and on rate constant for quenching of triplet, k_q, may be indicated by eq 5. The slopes of the curves in Figures 1 and 2

$$\varphi_0/\varphi = 1 + k_q[Q]/(k_{ir}[Am] + k_d) \quad (5)$$

equal $k_q/(k_{ir}[AM] + k_d)$, for quenching by piperylene, and, from the values of [AM] and k_d/k_{ir}, values of k_q/k_{ir} are calculated, Table II. They are lower for 2-naphthaldehyde than for 2-acetonaphthone, and lower in acetonitrile than in benzene. This indicates higher values of k_{ir} for the aldehyde than for the ketone, and higher values of k_{ir} in the dipolar solvent than in the hydrocarbon. Unfortunately we do not know the absolute value of k_q for piperylene in these systems. The triplet energies of 2-acetonaphthone and 2-naphthaldehyde are ~59 kcal,[28] while those of cis- and trans-piperylene are ~57 and 60 kcal,[32] respectively. The piperylene appeared to be only $^1/_{15}$th as effective as cyclohexadiene in quenching, and study with cyclohexadiene was complicated, apparently by its dimerization. If quenching by cyclohexadiene is diffusion controlled, $k_q \sim 6 \times 10^9$ M^{-1} sec^{-1}, k_q for piperylene may be ~4 $\times 10^8$ M^{-1} sec^{-1}. Values of k_{ir} and k_d may thus be estimated and are listed in Table II. For the most efficient reaction, photoreduction of 2-naphthaldehyde by triethylamine in acetonitrile, k_{ir} has a fairly high value, ~8 $\times 10^6$ M^{-1} sec^{-1}, similar to those for fluorenone[7] and p-aminobenzophenone[6] with triethylamine

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in hydrocarbons, and for benzophenone with primary amines,[2,5,29] but two orders of magnitude less than for benzophenones with tertiary amines.[5,33] Values for k_{ir} for 2-naphthaldehyde with triethylamine in benzene and for 2-acetonaphthone in both nonpolar and polar solvents are low, $1-6 \times 10^5 M^{-1} \sec^{-1}$, lower even than for the direct abstraction of hydrogen by benzophenones from alcohols. Since abstraction from alcohols is less easy than abstraction from amines, the inertness of the naphthyl carbonyl compounds to alcohols is readily understood. The naphthyl carbonyl compounds also show low values of k_d (see Table VI, ref 34), less than $10^4 \sec^{-1}$, more than an order of magnitude less than k_d for benzophenone.[34] Although these results are derived from the estimated low values of k_q for piperylene in these systems, it seems true that the π,π^* triplets of the naphthyl carbonyl compounds show relatively high stability and lifetimes, and low electrophilic reactivity.

The photoreduction of the naphthyl carbonyl compounds by triethylamine was not quenched appreciably by DABCO and by aniline despite their low ionization potentials. This result was unexpected since these compounds quench efficiently photoreduction of fluore-

none by triethylamine.[26] That fluorenone is both photoreduced and quenched by DABCO, while the naphthyl carbonyl is neither photoreduced nor quenched appreciably, may support the proposal that both processes proceed via a common pathway. This may be a CT complex, eq 1, or a less readily described transition in which charge transfer and partial hydrogen transfer are involved. Subtle effects of structure on reactivity may not be apparent in reactions of highly reactive n,π^* triplets, while π,π^* triplets may better reveal such differences. They are generally less electrophilic[14] and react best with strongly electron-donating tertiary amines, less well with secondary and primary amines, and little if at all with alcohols. High triplet energies, as of p-aminobenzophenone, and features in the carbonyl compounds which stabilize radical anion structure, such as the potential cyclopentadienide character of fluorenone, favor interactions with electron donors which may lead to both photoreduction and quenching. Dipolar solvents favor such interactions and may increase reactivity if they do not decrease intersystem crossing.

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The Beckmann–Chapman Rearrangement in the Solid State of Oxime Picryl Ethers[†,1]

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Abstract: The picryl ethers (1a-c) of benzophenone oxime and its syn and anti para bromo derivatives have been found to undergo a thermal Beckmann-Chapman rearrangement to give the N-picrylbenzanilides (3a-c, respectively); the product in each case is that formed by migration of the aromatic ring trans to the picryloxy group of the starting molecule. The reactions of 1b,c follow approximately first-order kinetics and are slower than estimated rates in solution by factors of 5-15. A vapor-phase rearrangement in small pockets of vapor in equilibrium with the solid cannot account for the reaction. Differential thermal analysis (dta) studies of the picryl ethers and their mixtures with the rearrangement products show that reaction occurs well below the eutectic temperature in each case. ΔH for these reactions is of the order of -80 kcal/mol. The observation of the rearrangement of heated single crystals shows initial formation of solid solutions of product (15-30%) in the starting material matrix and subsequent separation of microcrystallites 10^3 Å in diameter and randomly oriented with respect to the original axes. Larger crystals undergo cracking during the initial stages of rearrangement due to strains introduced by buildup of product in the matrix of starting material; the cracking appears to have a catalytic effect on the rearrangement. The implications of the crystal structures with respect to these rearrangements are discussed.

I n spite of a steady increase of interest in organic reactions in the solid state[4] relatively little is known about the mechanistic details of thermally induced intramolecular rearrangements of molecular crystals.

The thermal Beckmann–Chapman rearrangement[5] of benzophenone oxime picryl ether (1a) to N-picrylbenz-

† Figure 3 of this paper appears on p 879.
(1) Taken from the Ph.D. Thesis of J. D. McCullough, Jr., submitted to the University of Illinois, Urbana, Ill., 1970.
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(3) Alfred P. Sloan Research Fellow, 1968-1970.

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